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Loop reactor staged with structured fibrous catalytic layers for liquid-phase hydrogenations

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Abstract

A novel concept of a recycle loop reactor is developed with structured filamentous catalysts integrated as trays in a staged bubble column. The reactor can be operated in batch or continuous mode. Woven fabrics of activated carbon fibres (ACF) were used as support for the Pd catalyst.

The loop reactor was tested in the 2-butyne-1,4-diol hydrogenation showing selectivity up to 97% towards 2-butene-1,4-diol at conversions up to 80%. The reactor behaviour was described quantitatively assuming an ideally mixed reactor and Langmuir–Hinshelwood kinetics with weak hydrogen adsorption.

Catalyst reuse was demonstrated in multiple runs over a period of 6 months with more than 375 h on stream.

Keywords: Bubble columns; Catalysis; Catalyst support; Filamentous active carbon; Hydrogenation; Multiphase reactor

1. Introduction

During the last decades there has been a growing interest in catalytic reactor engineering useful in three-phase reactions. One of the main problems in performing reactions in liquid phase over solid catalysts is the avoidance of transport limitations. If the rate of transport within the liquid to the catalytic surface determines the reaction rate, it leads to large reactor dimensions. It may also drastically influence selectivity due to formation of undesired by-products. The rate of transport to the catalytic surface strongly depends on the particle diameter. Therefore, small size catalytic particles are required leading to the use of suspension "loop-type" reactors (Henkel, 2003). The minimum size of these particles is, however, limited by separation problems of the catalyst from the liquid after the reaction. Therefore, structured catalysts made from fibre materials present a valuable alternative for the multi-phase reactor design (Kiwi-Minsker et al., 1999; Höller et al., 2000b; Höller et al., 2001a).

The present study is aimed at the development of the active carbon fibre catalysts and their application in the loop reactor design. The selective liquid-phase hydrogenation of 2-butyne-1,4-diol to the corresponding butenediol was chosen as a model of the three-phase reaction. 2-butene-1,4-diol is an important intermediate for the fine chemical industry. It is used in the preparation of pharmaceuticals, like endosulfan and pyridoxine (vitamin B_6) and several insecticides. It also has wide-ranging applications in the paper and textile industries and in the manufacture of resins. Commercially, 2-butene-1,4-diol (B2) is obtained via the selective hydrogenation of 2-butyne-1,4-diol (B3). The reaction is usually carried out in an aqueous solution at elevated pressures (Hort and Graham, 1962; Hoffmann et al., 1974). The reaction network (Winterbottom et al., 1997) is schematically presented in Fig. 1, showing that the target product, 2-butene-1,4-diol, is an intermediate and can undergo further hydrogenation to give the saturated product (B1). Due to the possible double bond migration and hydrogenolysis of 2-butene-1,4-diol,

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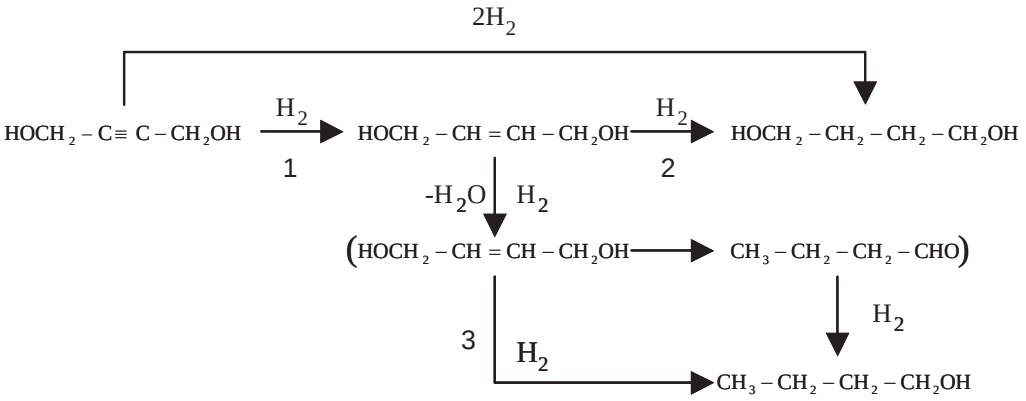

Fig. 1. Reaction scheme for hydrogenation of 2-butyne-diol.

further by-products like butyraldehyde, *n*-butanol and acetal may be formed in this reaction (Telkar et al., 2001). When supported palladium is used as a catalyst (Gouge, 1951; Hort and Graham, 1962; Hoffmann et al., 1974), mainly *cis*-2-butene-1,4-diol is formed, but its selectivity is a function of temperature, catalyst loading, solvent, addition of base, metal additives and catalyst support. In general, the variation in selectivity is due to a change of the rate of hydrogenation relative to the rate of mass transfer, and the rate of triple bond hydrogenation (of acetylene alcohol) relative to that of a double bond (olefin alcohol).

Recently we reported a new concept of the reactor with a structured catalytic bed for performing multiphase reactions (Kiwi-Minsker et al., 1999; Höller et al., 2000a; Höller et al., 2001b,c,d). The reactor is designed as a bubble column staged with trays of filamentous catalytic materials. Filamentous woven cloths, made of different types of glass and composite mixed oxides (Kiwi-Minsker et al., 1999), were used as supports for the deposition of active components: Pt, Pd, oxides of transition metals, etc. These types of catalysts should be classified as arranged catalysts (Cybulski and Moulijn, 1998). They were tested for intrinsic activity/selectivity in liquid-phase hydrogenation of benzaldehyde to toluene (Kiwi-Minsker et al., 1999), nitrobenzene to aniline (Perez et al., 1997; Höller et al., 2000a,b) and nitrite ions in water to nitrogen (Höller et al., 2001c). The palladium-based catalysts demonstrated high efficiency in these model reactions. The hydrodynamics in the bubble column staged with filamentous glass fabrics (cold model of the structured multiphase reactor) was also studied (Höller et al., 2001b; Höller et al., 2003). The reactor was shown to have a low-pressure drop during a fluid passage through the catalytic bed, redistribution of gas and liquid phases on each layer and narrow residence time distribution. Thus, this reactor design has shown an improved performance in multi-phase reactions.

In the present study woven fabrics of activated carbon fibres (ACF) were used as support for the Pd catalyst. These supports have advantageous characteristics and have been proven to have a great potential as catalytic supports, especially for expensive noble metals, since a high metal dispersion can be achieved via impregnation.

Kinetic studies of the selective hydrogenation of 2-butyne-1,4-diol were carried out with the Pd/ACF catalysts integrated in a self-gassing hollow shaft stirrer in a bench scale autoclave (Joannet et al., 2002). A kinetic model was developed assuming Langmuir–Hinshelwood mechanism and weak hydrogen adsorption allowing correct description of the experimental results. The Pd/ACF showed butenediol selectivity of $\geqslant$97% up to 90% conversion at 20–70 °C and hydrogen pressure up to 20 bar. Catalyst multiple reuse with stable activity/selectivity was demonstrated.

Nevertheless, the amount of the catalyst, which can be integrated in a stirrer is limited. Furthermore, the mass of catalyst per volume decreases with increasing volume of the stirred tank reactor leading to reduced specific reactor performances. Therefore, in this study we replaced the tank reactor by a loop reactor with an integrated bubble column staged by the catalyst layers of Pd/ACF. This arrangement allows obtaining higher catalyst packing as compared to a stirred tank reactor.

2. Experimental

2.1. Catalyst preparation

Fabrics of activated carbon fibres (Taiwan Carbon Technology Co) were used as supports for catalyst preparation. The fabrics are woven from the long threads of ca. 0.5 mm in diameter (Fig. 2a). These threads consist of a bundle of elementary filaments of 3–5 μm in diameter as shown in Fig. 2b. The palladium deposition on ACF was carried out via ion exchange from aqueous solution of Na_2PdCl_4 as described previously (Joannet et al., 2002). The loading of palladium was determined by atomic absorption spectroscopy, and the catalysts were characterized via BET-method for SSA and pore size distribution. Pulse chemisorption of

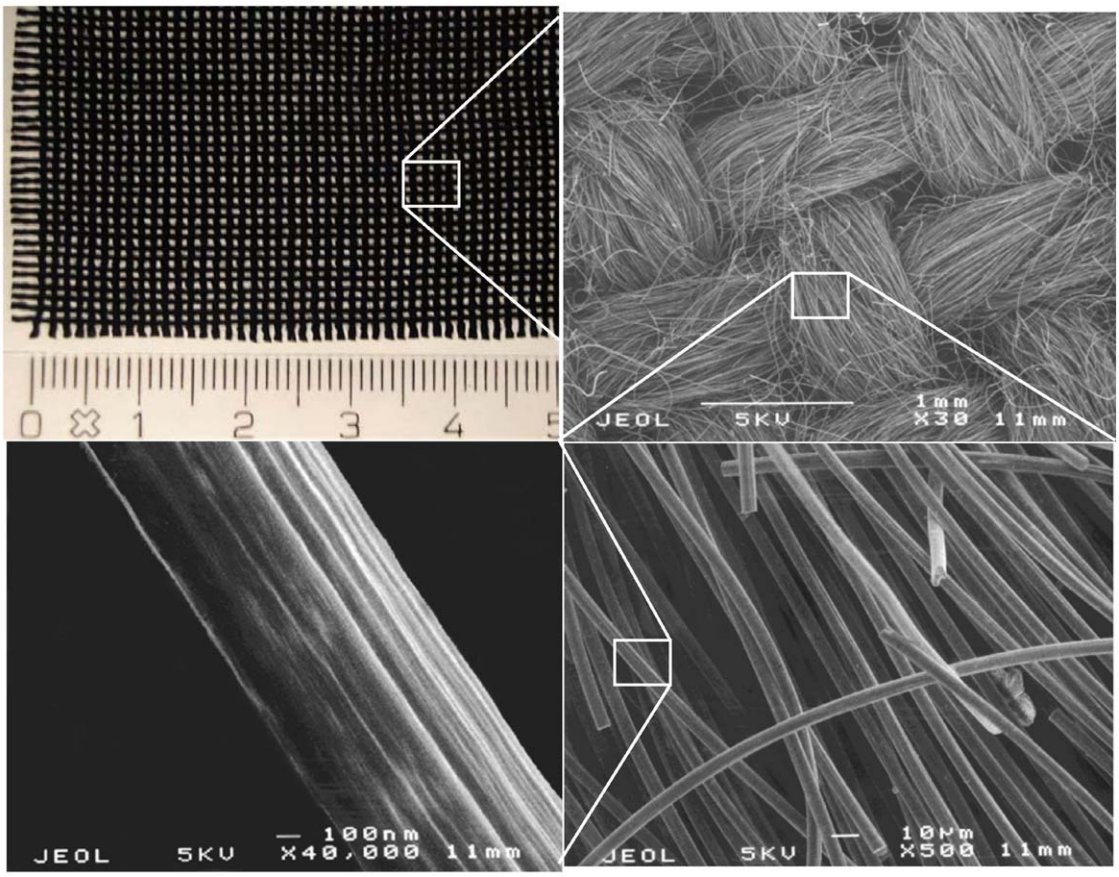

Fig. 2. Structure of woven active carbon fibres support (SEM).

carbon monoxide was applied for the determination of Pd dispersion.

In the present study, ACF support was loaded with 4 wt% Pd and this catalyst (4%Pd/ACF) was used throughout the study. Pd dispersion was found to be 22%, which corresponds to the mean diameter of 5.2 nm of the Pd particles.

2.2. Experimental set-up

A structured column staged with catalytic trays was designed and integrated in a loop system as shown in Fig. 3. The liquid phase is saturated with hydrogen in an autoclave with a volume of 1.15×10^{-4} m^3. During the rigorous mixing of 2000 rpm, an emulsion containing ca. 20 vol% of hydrogen is formed and pumped into the bubble column. The column with an inner diameter of 40 mm and a total height of 91 mm can house up to 20 trays of the catalyst layers. The Pd/ACF catalyst is fixed in between coarse metal grids to reduce mechanical stress and destruction of the ACF fabrics (Fig. 3). The gas is redistributed on each tray assuring high gas–liquid transfer. The loop reactor can be operated in batch mode or continuously at constant hydrogen pressures up to 20 bar.

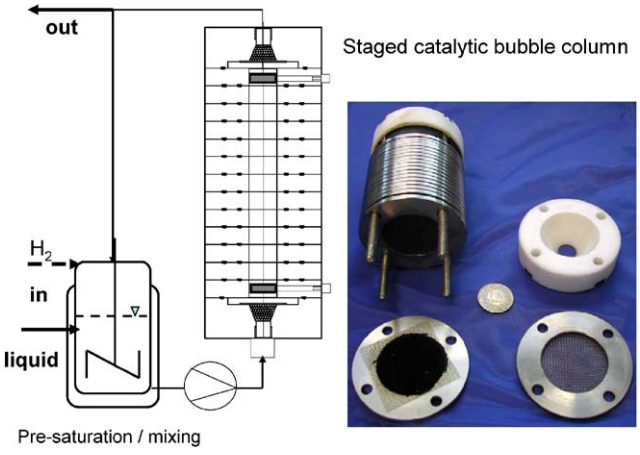

Fig. 3. Schematic diagram of the experimental set-up (left) and photo of the staged bubble column (right).

2.3. Product analysis

Samples of liquids withdrawn from the loop are analysed by gas chromatography (Auto System XL, PERKIN ELMER) with He as a carrier gas and FID-detector. Product separation was performed on a 30 m Perkin Elmer Elite

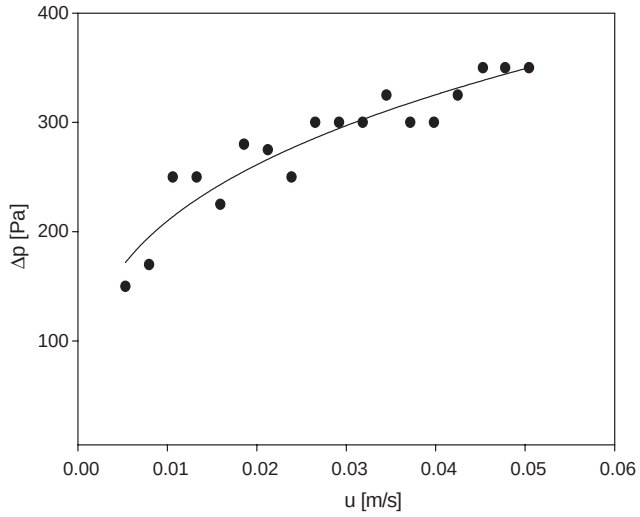

Fig. 4. Pressure drop over one catalytic layer as function of the superficial velocity.

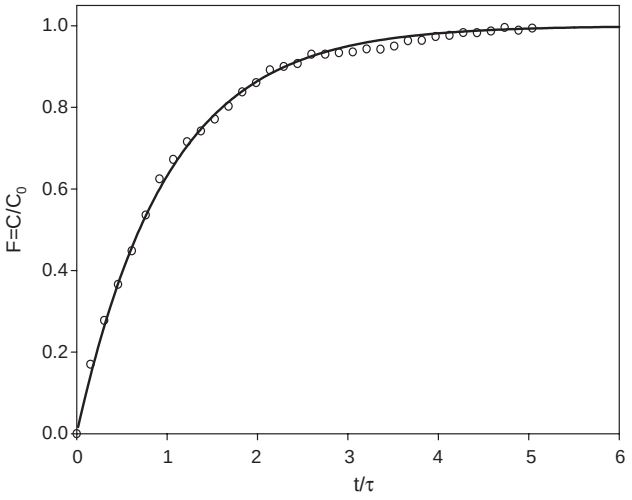

Fig. 5. Residence time distribution in the loop reactor. Recycle ratio $\phi = 200$.

Series 0.25 mm capillary column with a 0.25 μm coating, at temperature ramp of 20 °C min^{-1} from 100 to 220 °C. Butan-1,3-diol was used as the internal standard for quantitative GC analysis.

The initial reaction rate was used as a characteristic of catalytic activity, r_0[kmol kg$_{Pd}^{-1}$ s^{-1}]. The selectivity towards 2-butene-1,4-diol was calculated as

$$S_i = \frac{c_i}{\sum c_i}$$

with $i =$ the reaction products.

3. Results and discussion

3.1. Hydrodynamics and pressure drop

The fractional pressure drop Δp was measured in the structured catalytic column containing 10 layers as function of the flow-rate of the gas–liquid emulsion with a gas hold-up of 20%. In Fig. 4, the pressure drop over one catalytic layer is presented as a function of the linear velocity. The pressure drop strongly depends on the width between the threads of the fabrics and increases with the linear velocity of the liquid and the gas (Höller et al., 2000b). In the present study the pressure drop increases as

$$\Delta p = \text{const}\, u_{L,G}^{b} \quad (1)$$

with $u_{L,G}$ the superficial velocity of the gas–liquid mixture. The exponent $b = 0.31$ is identical to the value found by Höller et al. (2000b) and confirms the validity of the proposed empirical relationship.

3.2. Residence time distribution (RTD)

Under reaction conditions, liquid RTD was determined by changing the concentration of a tracer (butan-1,3-diol) at the entrance of the continuously operated loop reactor. By measuring the tracer concentration as function of time, the liquid RTD (F-curve) was obtained.

For the experimental conditions with an inlet feed of $0.06 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1} < Q_0 < 0.25 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1}$ and a recycle flow of $8 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1} < Q_r < 50 \times 10^{-6}\,\text{m}^3\text{s}^{-1}$, the recycle ratio was always $Q_r/Q_0 \geqslant 200$. Therefore, hydrodynamic behaviour corresponding to an ideally mixed continuous reactor can be expected. This was confirmed by the residence time distribution measurements. In Fig. 5 the response curve to a stepwise increase of a tracer concentration at the inlet of the loop reactor is shown. The RTD can be quantitatively described by a continuously operated ideally mixed reactor with

$$F = c/c_0 = 1 - \exp(-t/\tau). \quad (2)$$

3.3. Hydrogenation in a loop reactor operated in batch mode

The loop reactor was first used in a batch mode for a series of consecutive runs over a period of 6 months. Between the different hydrogenation reaction runs the catalyst was washed with de-ionised water and kept in hydrogen-saturated water to prevent deactivation of Pd. All runs were carried out at 30 °C and at constant hydrogen pressure of 0.68 MPa. In total 13 catalyst layers (1.37 g) were introduced in the reactor column. The flow rate in the recycle loop was varied between 8×10^{-6} and $60 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1}$, corresponding to a superficial velocity of $6.4 \times 10^{-3} - 48 \times 10^{-3}\,\text{m}\,\text{s}^{-1}$. The kinetics was found to be independent of the recycle flow,

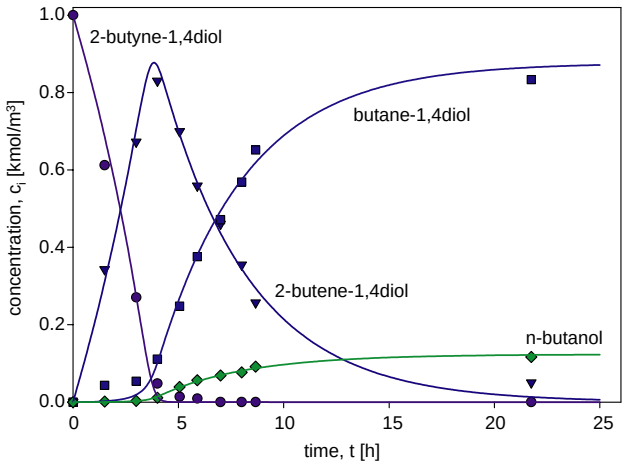

Fig. 6. Measured and predicted reactant and product concentrations as function of time (fresh catalyst).

therefore, external mass transfer resistance can be neglected under the used reaction conditions.

A typical plot of reactant and product concentrations as a function of time for a fresh catalyst is shown in Fig. 6. Within the first 3.5 h, the butynediol concentration decreases nearly linearly with time suggesting zero order towards butynediol. At the same time the concentration of butenediol increases and passes through the maximum at a reaction time of 4 h, corresponding to a butynediol conversion of about 95%. The initial selectivity towards butenediol is close to 100%. The supposed intermediates crotylalcohol and *n*-butyraldehyde were not found during the experiments, probably due to their low concentrations. Therefore, only a direct hydrogenation of butenediol to *n*-butanol (reaction 3) is suggested as a consecutive step in the reaction network, leading to undesired by-products.

In our previous work, the kinetics of the butynediol hydrogenation over the same catalyst was studied in an autoclave (Joannet et al., 2002). Linear dependency of the reaction rate as a function of hydrogen pressure was found in the pressure range from 0.1 to 2 MPa, whereas the reaction rate followed a zero order with respect to butynediol in the concentration range between 0.2 and 1 kmol m^{-3}. At higher butynediol concentrations, a decrease of the hydrogenation rate is observed (Chaudhari et al., 1987, 2001; Winterbottom et al., 2003). The observations can be rationalised on the bases of a Langmuir–Hinshelwood model assuming competitive adsorption of the reactants and a bimolecular reaction of the adsorbed species.

Based on the reaction scheme presented in Fig. 1 and neglecting the adsorption of water on the active sites, the transformation rate of butynediol can be expressed as follows

$$r_1 = \frac{k_1' K_{B3} C_{B3} K_{H_2} C_{H_2}}{[1 + K_{H_2} C_{H_2} + K_{B3} C_{B3} + K_{B2} C_{B2} + K_{B1} C_{B1} + K_B C_B]^2}. \quad (3)$$

The hydrogen concentration under reaction conditions is in the order of 5×10^{-3} kmol m^{-3} (Chaudhari et al., 1987). Therefore, the adsorption term for hydrogen can be neglected in the denominator. As the adsorption equilibrium constants of the olefinic and aliphatic products are small compared to the adsorption constant of the acetylenic reactant, a unique value is proposed, thus, reducing the number of adjustable model parameters. The resulting simplified kinetic model is presented in

$$r_1 = \frac{k_1 C_{B3}}{[1 + K_{B3} C_{B3} + K(C_{B2} + C_{B1} + C_B)]^2} \quad (4)$$

with $k_1 = k_1' K_{B3} K_{H_2} C_{H_2}$, and $K \cong K_{B2} \cong K_{B1} \cong K_B$.

For the consecutive reactions leading to butanediol and *n*-butanol analogical expression can be developed

$$r_2 = \frac{k_2 C_{B3}}{[1 + K_{B3} C_{B3} + K(C_{B2} + C_{B1} + C_B)]^2}, \quad (5)$$

$$r_3 = \frac{k_3 C_{B2}}{[1 + K_{B3} C_{B3} + K(C_{B2} + C_{B1} + C_B)]^2}. \quad (6)$$

The mass balances for butynediol and the reaction products are given by the following differential equation:

$$\frac{dC_{B3}}{dt} = -\frac{m_{cat}}{V_L} r_1, \quad (7)$$

$$\frac{dC_{B2}}{dt} = \frac{m_{cat}}{V_L} (r_1 - r_2 - r_3), \quad (8)$$

$$\frac{dC_{B1}}{dt} = \frac{m_{cat}}{V_L} r_2, \quad (9)$$

$$\frac{dC_B}{dt} = \frac{m_{cat}}{V_L} r_3. \quad (10)$$

Eqs. (7)–(10) were solved numerically with a Rosenbrock method using Berkeley Madonna Software (Macey and Oster, 1997–2001). The model parameters were estimated by fitting the simulated curves to the experimental data.

The proposed kinetic model describes the experimental data quite satisfactorily as can be seen from Figs. 6 and 7. The error between the experimental and simulated data is in the range of 15%. The adsorption equilibrium constant of butynediol is found to be two orders of magnitude higher compared to those of the products: $K_{B3}/K = 100$.

The stability of the catalyst was tested by using the same sample, Pd(4)/ACF, in a series of successive reaction runs over a time period of 6 months. After each run, the catalyst was cleaned by pumping de-ionised water through the reactor for 3–6 h corresponding to several mean residence times. In Fig. 7 the concentration profiles in the loop reactor after more than 375 h of operation are shown. The activity, characterised by the initial reaction rate, is approximately 5 times smaller compared to the fresh catalyst, whereas the selectivity for 2-butene-1,4-diol increases from 93% to 97%. This is shown in Fig. 8, where the selectivity and yield of the target product for the fresh and used catalyst is plotted

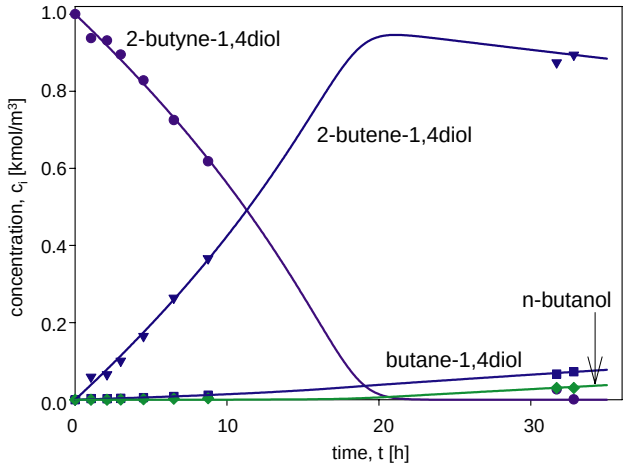

Fig. 7. Measured and predicted reactant and product concentrations as function of time (catalyst, used for 375 h).

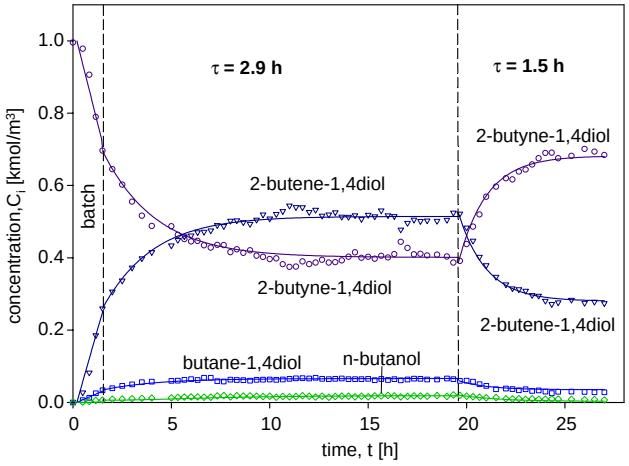

Fig. 9. Measured and predicted reactant product concentration as function of time. Continuous operated loop reactor.

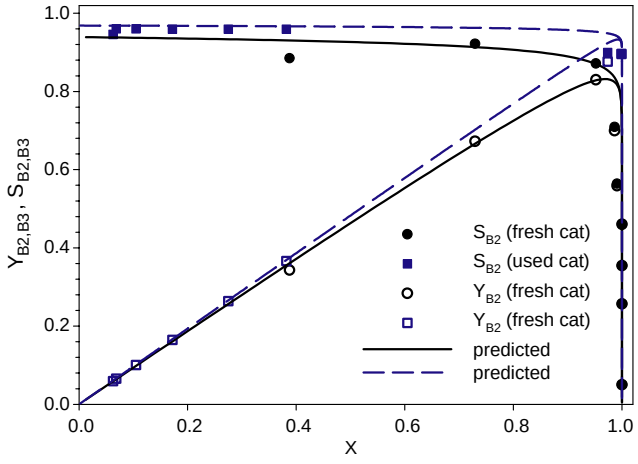

Fig. 8. Measured and predicted selectivity and yield of 2-butene-1,4 diol as function of conversion.

against the conversion of 2-butyne-1,4-diol. The increase of the selectivity may be explained by the diminishing of the most active sites, thus preventing the adsorption of 2-butene-diol and decreasing the rate of the consecutive reaction. The catalyst deactivation observed depends on the regeneration treatment (Joannet et al., 2002); therefore, a quantitative deactivation model is not available.

3.4. Continuous operation of the loop reactor

At concentrations higher than 1 kmol m^{-3}, a considerable decrease of the reaction rate with increasing 2-butyne-1,4-diol concentration and constant hydrogen pressure is observed (Chaudhari et al., 1987, 2001) and can be explained by the proposed Langmuir–Hinshelwood model (Eq. (3)). In consequence, highly specific reactor performances require low concentrations of 2-butyne-1,4-diol. Thus, the use of continuously operated mixed reactor is the most favourable reactor type. Therefore, the concept of the recycle reactor with an integrated staged bubble column was tested under reaction conditions corresponding to the batch operation mode: $T = 30\,^{\circ}C$, $p_{H2} = 0.68$ MPa. The bubble column was equipped with 10 layers of the Pd(4)ACF catalyst (0.93 g). The ratio between the recycling flow to the total feed was always kept higher than $Q_r/Q_0 \geqslant 200$. As demonstrated by the residence time distribution measurements, the loop reactor can be described by an ideal continuous stirred tank reactor model. The resulting mass balances for the liquid phase are summarised in the following equations:

$$\frac{dC_{B3}}{dt} = \frac{1}{\tau}(C_{B3,0} - C_{B3}) - r_1, \tag{11}$$

$$\frac{dC_{B2}}{dt} = -\frac{1}{\tau}C_{B2} + r_1 - r_2 - r_3, \tag{12}$$

$$\frac{dC_{B1}}{dt} = -\frac{1}{\tau}C_{B1} + r_2, \tag{13}$$

$$\frac{dC_B}{dt} = -\frac{1}{\tau}C_B + r_3. \tag{14}$$

In Fig. 9 the transient and the stationary behaviour of the continuous recycle reactor is presented. For the start-up, the reactor was operated batch-wise for 1.5 h. After this period a constant flow of 0.168×10^{-3} m^3 h^{-1} was introduced resulting in a reactor space–time of $\tau = 2.9$ h. The reactor reaches steady state after ca. 9 h. Butynediol conversion reaches 60% and a butenediol selectivity of 86% is obtained. Diminishing the space–time to $\tau = 1.5$ h leads to a reduced conversion of 32% and selectivity increases up to 90%. Based on the kinetic model, the transient and steady behaviour of the loop reactor can be quantitatively predicted (Fig. 9). Within the time of continuous reactor operation of 30 h, no deactivation is observed. The productivity of the continuously operated reactor was found to be 0.76 mol/(kg_{Pd} s).

4. Conclusion

- Activated carbon fibres (ACF) in the form of woven fabrics are shown to be suitable supports for the preparation of structured catalysts useful in three-phase hydrogenations.
- A novel concept of a recycle loop reactor is developed with structured Pd/ACF catalysts integrated as trays in a staged bubble column. The reactor can be operated in batch or continuous mode.
- The loop reactor was tested in the 2-butyne-1,4-diol hydrogenation showing selectivity up to 97% towards 2-butene-1,4-diol at conversions up to 80%. The reactor behaviour was described quantitatively assuming an ideally mixed reactor and Langmuir–Hinshelwood kinetics with weak hydrogen adsorption.
- Catalyst reuse was demonstrated in multiple runs over a period of 6 months with more than 375 h on stream.

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References

Chaudhari, R.V., Gholap, R.V., Emig, G., Hofmann, H., 1987. Gas–liquid mass transfer in “dead-end” autoclave reactors. Canadian Journal of Chemical Engineering 65, 744–751.

Chaudhari, R.V., Seayad, A., Jayasree, S., 2001. Kinetic modeling of homogeneous catalytic processes. Catalysis Today 66 (2–4), 371–380.

Cybulski, A., Moulijn, J.A. (Eds.), 1998. Structured Catalysts and Reactors. Chem. Ind. (Dekker), New York.

Gouge, M., 1951. Preparation des γ glycols ethyléniques primaires secondaires et primaires tertiaires. Ann. Chim. 12, 648–678.

Henkel, K.-D., 2003. Reactor Types and Their Industrial Applications. Ullmann’s Encyclopedia of Industrial Chemistry. Wiley-VCH, Weinheim.

Hoffmann, H., Boettger, G., Bör, K., Wache, H., Kräfje, H., Körning, W., 1974. Katalysator zur partiellen Hydrierung. BASF AG, D-6700 Ludwigshafen. De, 1, 139–832.

Höller, V., Wegricht, D., Yuranov, I., Kiwi-Minsker, L., Renken, A., 2000a. Three-phase nitrobenzene hydrogenation over supported glass fiber catalysts: reaction kinetics study. Chemical Engineering Technology 23 (3), 251–255.

Höller, V., Wegricht, L., Kiwi-Minsker, L., Renken, A., 2000b. Fibrous structured catalytic beds for three-phase reaction engineering hydrodynamics study in staged bubble columns. Catalysis Today 60, 51–56.

Höller, V., Radevik, K., Kiwi-Minsker, L., Renken, A., 2001a. Bubble columns staged with structured fibrous catalytic layers: residence time distribution and mass transfer. Industrial and Engineering Chemistry Research 40, 1575–1579.

Höller, V., Radevik, K., Kiwi-Minsker, L., Renken, A., 2001b. Bubble columns staged with structured fibrous catalytic layers: residence time distributions and mass transfer. Industrial and Engineering Chemistry Research 40, 1575.

Höller, V., Radevik, K., Yuranov, I., Kiwi-Minsker, L., Renken, A., 2001c. Reduction of nitrite-ions in water over Pd-supported on structured fibrous materials. Applied catalysis B 841, 1–8.

Höller, V., Yuranov, I., Kiwi-Minsker, L., Renken, A., 2001d. Structured multiphase reactors based on fibrous catalysts: nitrite hydrogenation as a case-study. Catalysis Today 69, 175–181.

Höller, V., Ruzicka, M., Drahos, J., Kiwi-Minsker, L., Renken, A., 2003. Acoustic and visual study of bubble formation processes in bubble columns staged with fibrous catalytic layers. Catalysis Today 151–157.

Hort, E.V., Graham, D.E., 1962. Verfahren zur partiellen Hydrierung von Butin-(2)-diol-(1,4) zu buten-(2)-diol-(1,4). General Aniline and Film Corp. New York, DE, 1, 139–832.

Joannet, E., Horny, C., Kiwi-Minsker, L., Renken, A., 2002. Palladium supported on filamentous active carbon as effective catalyst for liquid-phase hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol. Chemical Engineering Science 57, 3453–3460.

Kiwi-Minsker, L., Yuranov, I., Höller, V., Renken, A., 1999. Supported glass fibers catalysts for novel multi-phase reactor design. Chemical Engineering Science 54, 4785–4790.

Macey, R.I., Oster, G.F., 1997–2001. Berkeley Madonna, Version 8.0.1, www.berkeleymadonna.com.

Perez, M.M.C., Martinez de Lecea, S.C., Solano, L.A., 1997. Platinium supported on activated carbon cloths as catalyst for nitrobenzene hydrogenation. Applied Catalysis A 151, 461–475.

Telkar, M.M., Rode, C.V., Rane, V.H., Jaganathan, R., Chaudhari, R.V., 2001. Selective hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol: roles of ammonia, catalyst pretreatment and kinetic studies. Applied Catalysis a—General 216 (1–2), 13–22.

Winterbottom, J.M., Marwan, H., Viladevall, J., Sharma, S., Raymahasay, S., 1997. Influence of dispersity on the activity, selectivity and stability of raney nickel during the hydrogenation of 1,4-butynediol into 1,4-butanediol. Studies in Surface Science and Catalysis 108, 59–66.

Winterbottom, J.M., Marwan, H., Stitt, E.H., Natividad, R., 2003. The palladium catalysed hydrogenation of 2-butyne-1,4-diol in a monolith bubble column reactor. Catalysis Today 79 (1–4), 391–399.